Automation of liquid crystal phase analysis for SAXS

Stefan Paporakis[a], Jack Binns[a], Dilek Yalcin[b], Calum J. Drummond[a], Tamar L. Greaves[a], Andrew V. Martin[a,*]

[a] School of Science, College of STEM, RMIT University, 124 La Trobe Street, Melbourne, VIC 3000, Australia.
[b] CSIRO Manufacturing, Clayton, VIC 3168, Australia.

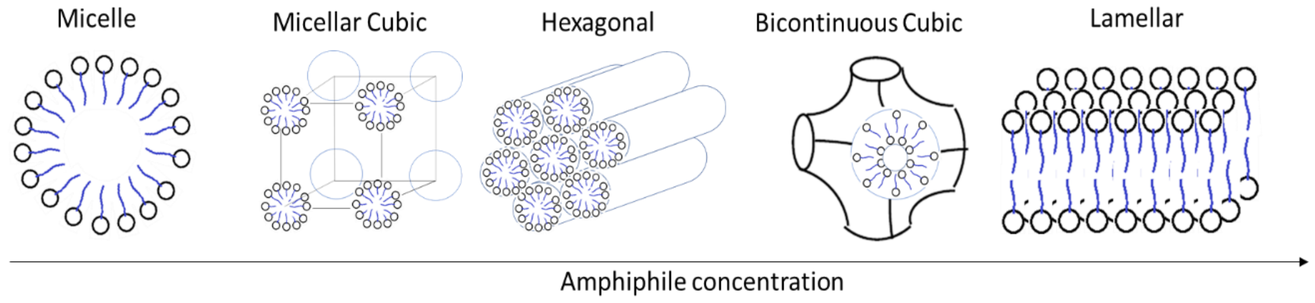
Introduction

Lyotropic liquid crystal phases (LCPs) are widely studied for diverse applications, including protein crystallization and drug delivery. The use of ionic liquids (ILs) as LCP mediators has been a topic of interest, as some ILs are found to support diverse LCPs. Many ammonium-based protic ILs (PILs) support LCPs[1]. Varying the solvent and temperatures can significantly alter LCP structures, however due to the large variability of PIL-solvent combinations that support LCPs, accurate phase identification requires collecting hundreds or thousands of SAXS profiles, each of which needs to be analysed individually and manually. Currently there are well established methods for high-throughput PIL synthesis, and for high throughput LCP data collection with small angle x-ray scattering (SAXS) synchrotron sources. Here we present a high-throughput LCP identification method which has been developed using an existing data set of 668 SAXS patterns of LCP patterns of CTAB in PIL containing solvents[2], extending the investigation further to 332 SAXS patterns of SDS in PIL containing solvents.

Liquid crystal phases in protic ionic liquids

How do we make liquid crystal phasess?

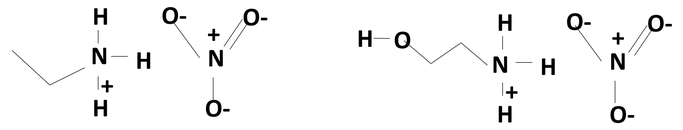
Induce aggregation and self assembly of amphiphiles. Performed by placing materials with hydrophobic and hydrophilic components in water and/or PIL solvents.



Protic ionic liquid-solvent liquid crystal phase samples

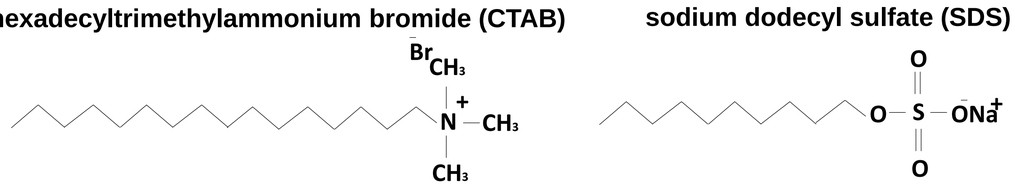
53 samples of EAN and EtAN in both CTAB and SDS solutes varying from stoichiometry. The high number of compositional variance makes the production of phase diagrams very difficult and time consuming when analysing 100s of patterns.

Ethylammonium nitrate (EAN) **Ethanolammonium nitrate (EtAN)**



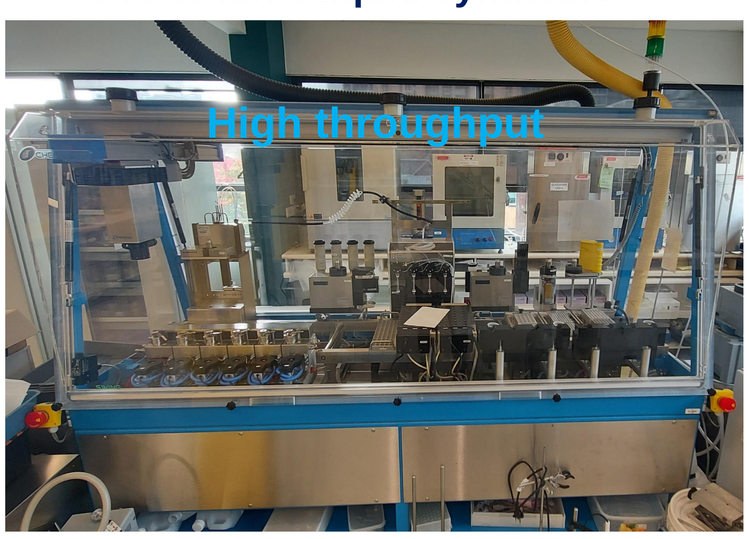
Amphiphile sample structures

hexadecyltrimethylammonium bromide (CTAB) **sodium dodecyl sulfate (SDS)**

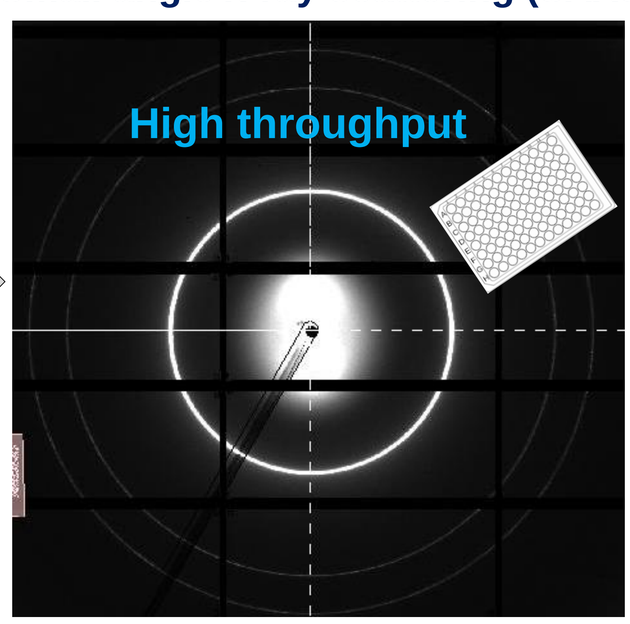


The bottleneck of liquid crystal phase analysis

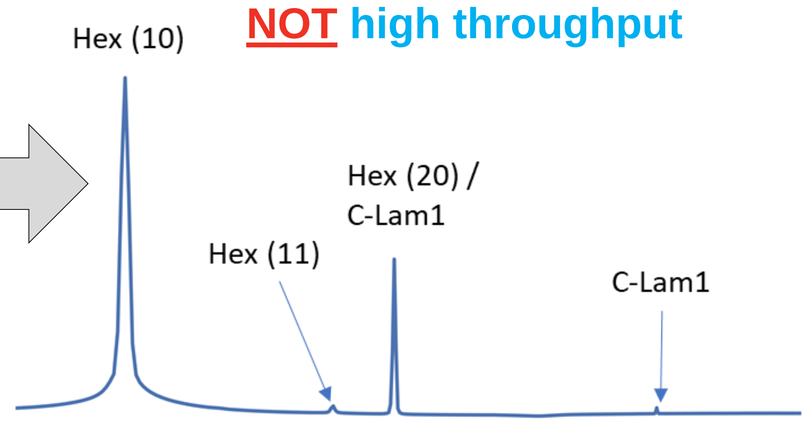
Protic ionic liquid synthesis



Small angle x-ray scattering (SAXS)

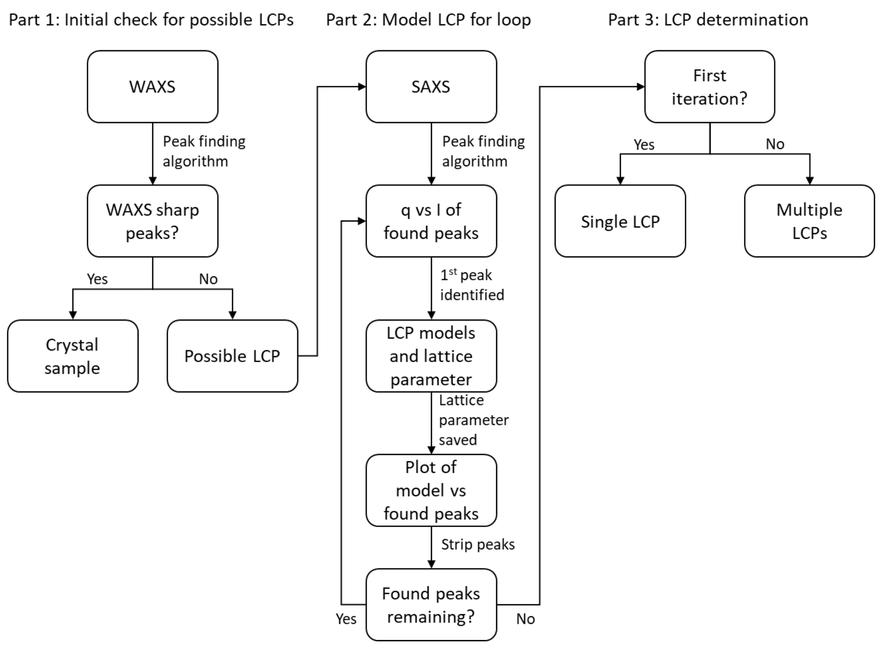


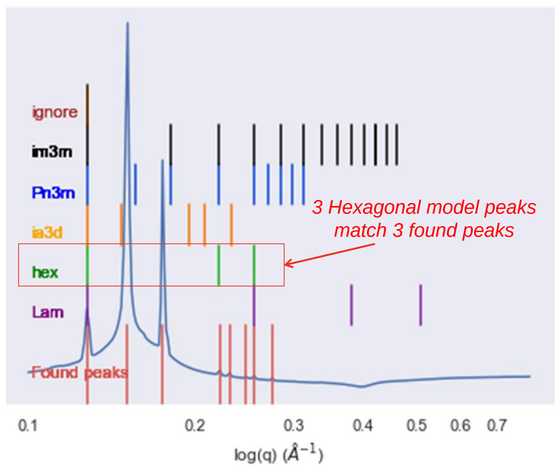
Liquid crystal phase identification



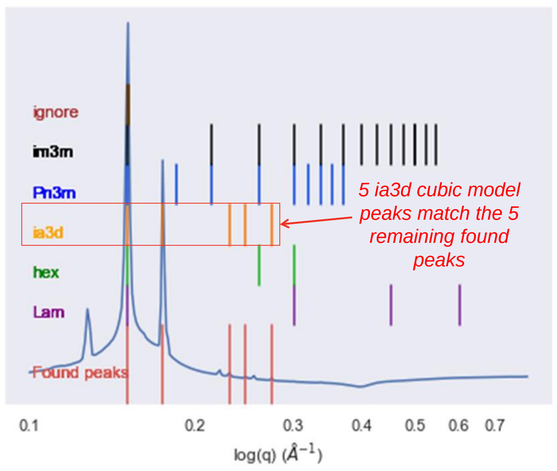
Our solution to the LCP analysis bottleneck

LCPs have known ratios of ring spacings. Therefore the distances between peaks in a scattering profile are also known ratios. We developed a high throughput identification procedure that identifies peaks in a scattering profile, then matches the found peaks to model LCP peak ratios.





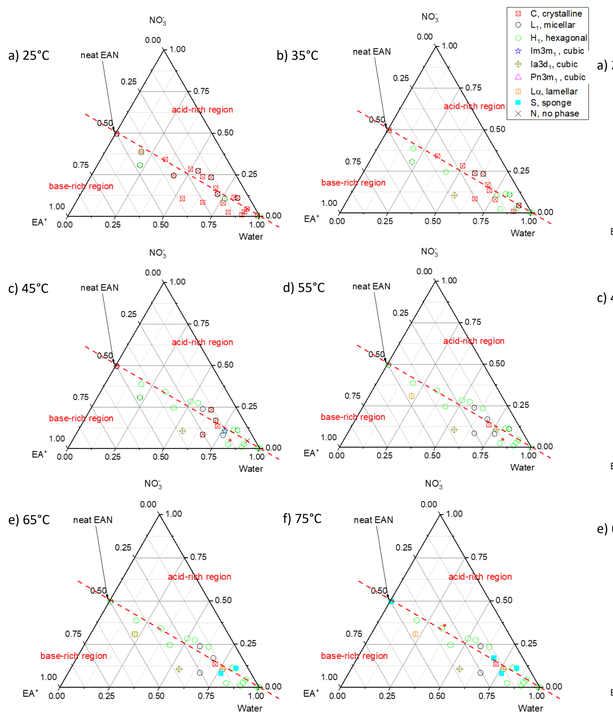
Found peak position (red) matched with theoretical peak positions of Lamellar (purple), Hexagonal (green), im3m cubic (black), pn3m cubic (blue) and ia3d cubic (yellow) phases.



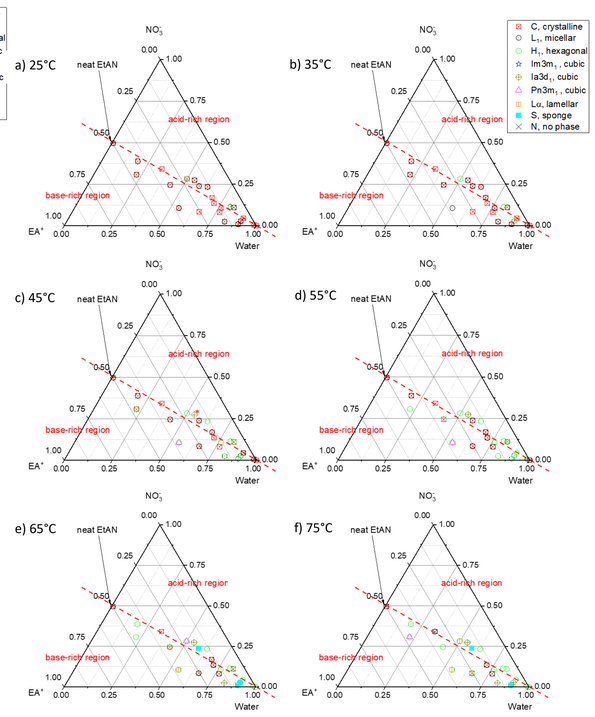
Hexagonal-LCP stripped SAXS profile

Phase diagram production

The automated identification procedure enabled the characterisation of single or multiple LCPs over 20 times faster than manual analysis methods with equivalent accuracy in the CTAB-PIL samples. Applying the procedure to SDS-EAN and SDS-EtAN produced novel phase diagrams.



Phase diagrams of 50 wt% SDS in EAN containing solvents from 25°C-75°C



Phase diagrams of 50 wt% SDS in EtAN containing solvents from 25°C-75°C

Summary

- **Intricate liquid crystal phases identified in a variety of protic ionic liquid solvents, shows phase diversity and solvent dependence of materials.**
- **Developed high throughput phase identification procedure on average over 20 times faster than manual analysis.**
- **Analysis bottleneck removed. Allows for more efficient experimentation on phase formation in ionic liquids**

[1] Greaves, T. L.; Weerawardena, A.; Fong, C.; Drummond, C. J. Formation of Amphiphile Self-Assembly Phases in Protic Ionic Liquids. *J. Phys. Chem. B* **2007**, *111* (16), 4082–4088.
[2] Yalcin, D.; Drummond, C. J.; Greaves, T. L., High throughput approach to investigating ternary solvents of aqueous non-stoichiometric protic ionic liquids. Phys. Chem. Chem. Phys. 2019, 21, 6810-6827.

Acknowledgements

The SAXS data presented here is a result of collaboration with the Australian Synchrotron and their SAXS/WAXS beamline team.